TITLE OF THE INVENTION

SILICA AND SILICATE BY PRECIPITATION AT CONSTANT ALKALI NUMBER, AND ITS USE

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

The invention relates to silicas and silicates obtained and obtainable by acid precipitation of alkali metal silicates at constant alkali number, and to their use, for example as carriers.

DISCUSSION OF THE BACKGROUND

Precipitated silicas as carrier materials, particularly for vitamin E acetate or choline chloride have long been known. For example, EP 0 937 755 describes how a precipitated silica is prepared by a pH-controlled precipitation reaction and then spray-dried. Precipitated silica prepared in this way is particularly suitable for use for adsorbing liquid active substances such as choline chloride solution or vitamin E, for example. DE 198 60 441 discloses how an active substance adsorbate may be prepared from a precipitated silica and an active substance by spraying or injecting a silica suspension together with one or more active substances into a fluidized bed generated using hot air. It is likewise possible to use hydrophobic precipitated silicas for these purposes, as described in DE 198 25 687.

In the context of their use as carriers, the following properties of silicas are important: adsorption capacity, good sorption kinetics, and low fine dust fraction. Owing to heightened safety requirements and the need to prepare adsorbates with ever higher concentrations, there is therefore a demand for carrier silicas which have a very low fines fraction with an adsorptiveness which is heightened at the same time.

OBJECTS OF THE INVENTION

The known silicas generally do not possess pronounced sorption characteristics for polar compounds. Since silicas are frequently used as carrier material for polar compounds such as choline chloride, propionic acid or formic acid, for example, it is one object of the present invention to provide a silica and a silicate which possesses particularly good sorbency for polar compounds.

SUMMARY OF THE INVENTION

It has surprisingly been found that by preparing precipitated silica and silicate at a constant alkali number, products can be obtained which have good sorption characteristics for polar compounds.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides such precipitated silicas and silicates as well as a process for preparing such materials comprising

- optionally providing an initial aqueous silicate solution
- simultaneously metering into an aqueous silicate solution or a vessel, etc., an aqueous silicate solution and a Lewis and/or Brønsted acid to provide a mixture
- reacidifying the mixture to a pH of 7-3.0
- optionally filtering, and
- optionally drying,

the metered addition (or mixing, etc.) of the aqueous silicate solution and the Lewis and/or Brønsted acid being carried out while maintaining a constant alkali number of at least 1.

Where an aqueous silicate solution is initially present it is generally different from the silicate solution metered in as concentrations generally differ due to the initial presence of water. See *infra*.

While not bound by theory it is believed that the high alkali number of the silicas and silicates of the invention, and the inventively prepared precipitated silicas and silicates, results in a high silanol group density and thus enhances a high absorbency for polar absorbates.

The present invention likewise provides for the use of the silicas and silicates of the invention as carrier material, for example for feed additives, chemical intermediates, or in the laundry detergent industry, for example.

It is possible to add an electrolyte prior to or during the simultaneous addition (or metering) of aqueous silicate solution and acid. Electrolytes for the purposes of the present invention are not limited and include metal salts or their aqueous solutions which are not incorporated into the amorphous SiO_2 structure, such as Na, K, Rb, Ba, in each case in sulfate, acetate, halide or carbonate form. The fraction of the electrolyte is 0.01-26% by weight (calculated as the metal ion) based on total weight of product silica or silicate.

It is likewise possible to add metal salts or their solutions which are incorporated into the SiO_2 structure to the precipitation mixture, so giving silicates. The fraction of these metal ions may be between 1 and 50, preferably 10% by weight based on total weight of silicate; customary ions are Al, Zr, Ti, Fe, Ca and Mg.

There are known preparation processes for precipitated silicas in the course of which a constant pH is maintained. A precipitation reaction at constant alkali number, on the other hand, means that the concentration of freely available alkali ions (e.g., sodium ions) is kept constant.

As a result of the acid-base reactions during the precipitation of waterglass with sulfuric acid, sodium ions are on the one hand released in the form of sodium sulfate; on the other hand, sodium ions are incorporated into the silicate agglomerates which form.

Since these two reactions proceed independently of one another kinetically, the course of precipitations at constant pH is different than that of precipitations conducted in accordance with the invention.

In the case of a precipitation reaction at constant alkali number, the pH changes analogously: for example, at a constant alkali number of 30, the pH falls from about 10.35 to levels between 8 and 10, depending on the duration of the precipitation reaction (simultaneous addition of alkaline silicate solution and acid). The longer such a precipitation reaction lasts, the lower the pH at the end of the reaction is. The intercalation of sodium ions into the silica structure is probably responsible for this.

The precipitated silicas and silicates of the invention are prepared at an alkali number of at least 1, in particular at least 15, preferably at an alkali number of from 15 to 60, with particular preference at an alkali number of from 25 to 50, and with very particular preference at an alkali number of from 30 to 40, including all of 2, 5, 10, 15, 20, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 45 and 55, the alkali number being kept constant during the precipitation reaction.

The alkali number (AN) is determined by measuring the consumption of hydrochloric acid in a direct potentiometric titration of the precipitation suspension at a pH of 8.3, i.e., the color change point of phenolphthalein. The consumption of hydrochloric acid is a measure of the free alkali content of the solution or suspension. Owing to the temperature dependency of the pH, this measurement is made at 40°C and after a waiting time of 15 minutes. A precise description of the measurement protocol is given in the examples.

The invention provides a precipitated silica, characterized by the following physicochemical data:

BET surface area	from 50 to 700 m^2/g with the preferential ranges 100-300 m^2/g, 150-220 m^2/g, 180-210 m^2/g,
DBP absorption	from 100 to 450 g/100 g with the preferential ranges 250-450 g/100 g, 280-450 g/100 g,
Choline chloride	from 50 to 400 g/100 g with the absorption preferential ranges 240-400g /100g, 280-400 g/100 g (75% by weight aqueous solution),
CTAB surface area	from 50 to 350 m^2/g with the preferential ranges 100-250 m^2/g, 130-200 m^2/g,

the ratio of the DBP absorption to the choline chloride absorption, as a measure of the adsorption of a nonpolar substance and of a polar substance, being less than 1.07, preferably less than 1.05, with very particular preference less than 1.03.

Since silicas or silicates possess different affinities for hydrophobic, i.e., nonpolar, and hydrophilic, i.e., polar, compounds, two measurements are necessary for complete characterization of this property. The DBP number is used as a measure of an affinity of silicas for hydrophobic compounds; the choline chloride absorption is used as a measure of the affinity of silicas for hydrophilic compounds. The ratio of these DBP/choline chloride absorption figures therefore reflects a new physical property.

The silicates or precipitated silicas of the invention may additionally be characterized by the modified Sears number. The modified Sears number is determined by the techniques described in the examples/methods and may be greater than 20, preferably greater than 25, with particular preference greater than 28. Preferably the modified Sears number is 45 or less.

The preferred aqueous silicate solution is sodium silicate solution; as the Brønsted acid, sulfuric acid, hydrochloric acid, carbonic acid or acetic acid may be used. As the Lewis acid it is possible to use Al^{3+} ions, in the form for example of the sulfate.

The BET surface area is determined in accordance with ISO 5794/1, Annex D, incorporated herein by reference, the CTAB surface area in accordance with ASTM D 3765-92, incorporated herein by reference, the DBP absorption in accordance with the protocol described in the annex.

The precipitated silica suspensions prepared by the process of the invention may be filtered conventionally and the filter cake may be washed with water. The filter cake obtained

in this way is liquefied, where appropriate, and may be dried by the customary drying process, such as rotary tube furnace, Büttner dryer, spin-flash dryer, pulse combustion dryer, spray dryer, or in a nozzle tower. Further, purely physical treatment by granulation and/or grinding is likewise possible. Also possible is a water repellency treatment or coating with waxes.

The silicates or precipitated silicas of the invention may be used in particular as carriers, for example for feed additives such as formic acid, propionic acid, lactic acid, phosphoric acid, choline chloride solution or plant extracts, tagatese extract for example.

Furthermore, the precipitated silicas of the invention may be used as carrier material for chemical intermediates such as melamine resins or coatings additives or in the laundry detergent industry as carriers for fragrances or detergents.

Moreover, the silicates or precipitated silicas of the invention may be used as a filler in elastomers/plastics, battery separators, toothpastes, catalyst supports, or as a flocculation assistant.

The following examples and measurement protocols are intended to illustrate the invention without restricting its scope.

Examples

General experimental protocol: (Example 1-8)

Water is charged to a precipitation vessel with a capacity of 2 m^3 (applies to all pilot-scale trials; laboratory trials: 40 l; plant trials: 80 m^3) and a certain amount of waterglass (i.e., sodium silicate solution) is metered in. The values for the density of the sodium silicate solution, sulfuric acid, the SiO_2 content, Na_2O content, temperature, and the alkali number (AN number) are evident from the tables. After the target temperature has been reached, sodium silicate solution and sulfuric acid are metered in. Thereafter, sulfuric acid continues to be metered in at the same rate until a pH of 3.5 is reached. The suspension with the described solids content is filtered on filter presses (membrane filter presses) and then prepared for drying. The filter cake is liquefied by adding sulfuric acid, using a shearing unit, until the desired viscosity and pH are reached. The feed is then dried.

List of abbreviations:

AN = alkali number

WGL charge = waterglass charge = initial charge of sodium silicate solution

WGL = waterglass

VA = time at which the viscosity increases sharply, also referred to as the gel point

Fc = precipitation rate in [mol/(l•min)], defined by

$$\frac{\text{ml/min (acid inflow)} \bullet \text{mol/l (acid molarity)}}{\text{l (initial charge)}}$$

% TS feed = % solids content of feed to dryer

GV-Din = loss on ignition to DIN

LF = conductivity

CC absorption = choline chloride absorption

Example	1	2	3	4
Trial No.	7508	7504	7487	7491
AN	30	40	40	40
Water charge (l)	1359	1220	1314	1220
WGL charge (l)	145.3	186.1	197.6	184.1
Temperature (°C)	85	85	85	85
WGL metered (l)	344.2	211.4	247.9	249.2
Acid metered (l)	26.32	16.42	19.32	20.15
VA (min)	22.50	37.00	38.50	41.00
Precipitation period (min)	60	55	55	65
Reacidification amount (l)	20.00	22.30	25.11	22.86
Reacidification time (min)	21		39	156
Fc	5.52	4.01	4.39	4.17
g/l (solids content of the earth suspension)	94.8	92.5	97.7	99.2
Waterglass analysis				
Density (g/ml)	1.346	1.346	1.349	1.349
% SiO_2	27.2	27.2	27.3	27.3
% Na_2O	7.99	7.99	8.08	8.08
Sulfuric acid (mol/l H_2SO_4)	18.14	18.14	18.14	18.14
Dryer	Nozzle tower dryer	Nozzle tower dryer	Nozzle tower dryer	Nozzle tower dryer
pH of feed	3.9	3.8	3.8	3.8
Viscosity (mPa*s)	40	75	110	120
% TS feed	17.3	18.3	19.7	20.3

Example	1	2	3	4
Analysis				
GV-DIN (%)	5.2	4.9	4.9	4.9
Water (%)	6.2	5.3	6.3	6.0
pH	6.5	6.5	6.9	6.1
LF (µS/cm)	610	600	550	650
N_2 surface area (m^2/g)	199	189	167	165
CTAB surface area (m^2/g)	148	127	120	113
DBP number (g/100 g) (corrected, i.e., for anhydrous material)	279	281	270	270
Sears number (V2)	31.3	30.9	29.4	29.5
CC absorption	276	282	270	275
Ratio of DBP/CC absorption	1.0109	0.9965	1.0000	0.9818

Example	5	6	7	8
Trial No.	7397	7362	7370	7420
AN	20	30	30	40
Water charge (l)	1651	1499	1459	1224
WGL charge (l)	108.4	148.8	148.8	185.3
Temperature (°C)	85	85	85	85
WGL metered (l)	345.0	441.8	542.5	224.4
Acid metered (l)	28.40	36.00	32.78	18.44
VA (min)	24.75	27.75	27.25	40.25
Precipitation period (min)	40	65	60	60
Reacidification amount (l)	20.42	28.41	24.70	26.37
Reacidification time (min)	41	63	56	94
Fc	7.21	5.96	6.03	3.86
g/l (solids content of the earth suspension)	79.3	104.0	100.0	92.5
Waterglass analysis				
Density (g/ml)	1.346	1.348	1.348	1.351
% SiO_2	27.4	27.2	27.2	27.6
% Na_2O	8.03	8.02	8.02	8.01
Sulfuric acid (mol/l H_2SO_4)	18.87	17.74	17.64	17.70
Dryer	Nozzle tower dryer	Nozzle tower dryer	Nozzle tower dryer	Nozzle tower dryer
pH of feed	3.6	3.6	3.4	3.6
Viscosity (mPa*s)	75	60	33	90
% TS feed	16.3	16.9	15.3	19.8

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Example	5	6	7	8
Analysis				
GV-DIN (%)	5.1	5.3	5.8	5.6
Water (%)	5.8	6.2	5.0	5.9
pH	6.8	6.7	6.3	6.6
LF (µS/cm)	490	510	530	550
N_2 surface area (m^2/g)	240	175	185	137
CTAB surface area (m^2/g)	200	135	148	115
DBP number (g/100 g) (corrected, i.e., for anhydrous material)	247	293	292	276
Sears number (V2)	31.0	31.5	30.8	28.5
CC absorption	233	285	294	279
Ratio of DBP/CC absorption	1.0601	1.0281	0.9932	0.9892

Example	Hubersil 5170 9	HiSil SC72 10	Sipernat 22 11	Sipernat 2200 12
Trial No.				
AN				
Water charge (l)				
WGL charge (l)				
Temperature (°C)				
WGL metered (l)				
Acid metered (l)				
VA (min)				
Precipitation period (min)				
Reacidification amount (l)				
Reacidification time (min)				
Fc				
g/l (solids content of the earth suspension)				
Waterglass analysis				
Density (g/ml)				
% SiO_2				
% Na_2O				
Sulfuric acid (mol/l H_2SO_4)				
Dryer	Granulation	Nozzle tower dryer	Spray dryer	Nozzle tower dryer
pH of feed				
Viscosity (mPa*s)				
% TS feed				

Example	Hubersil 5170 9	HiSil SC72 10	Sipernat 22 11	Sipernat 2200 12
Analysis				
GV-DIN (%)				
Water (%)	6.0	5.7	5.0	5.0
pH				
LF (µS/cm)				
N_2 surface area (m^2/g)				
CTAB surface area (m^2/g)				
DBP number (g/100 g) (corrected, i.e., for anhydrous material)	204	311	270	255
Sears number (V2)	18.4	23.5		
CC absorption	165	270	235	231
Ratio of DBP/CC absorption	1.2364	1.1519	1.149	1.1039

Determining the modified Sears number of silicas, silicates and hydrophobic silicas

1. Scope

Free OH groups are detectable by titration with 0.1 N KOH in the range from pH 6 to pH 9.

2. Apparatus

2.1 Precision balance to 0.01 g precisely

2.2 Memotitrator DL 70, Mettler, equipped with 10 ml and 20 ml buret, 1 pH electrode and 1 pump (e.g., NOUVAG pump, type SP 40/6)

2.3 Printer

2.4 Titration vessel 250 ml, Mettler

2.5 Ultra-Turrax 8000-24,000 rpm

2.6 Thermostated waterbath

2.7 2 dispenser 10-100 ml for metering methanol and deionized water

2.8 1 dispenser 10-50 ml for metering deionized water

2.9 1 measuring cylinder 100 ml

2.10 IKA universal mill M20

3. Reagents

3.1 Methanol p.a.

3.2 Sodium chloride solution (250 g NaCl p.a. in 1000 ml deionized water)

3.3 0.1 N hydrochloric acid

3.4 0.1 N potassium hydroxide solution

3.5 Deionized water

3.6 Buffer solutions pH 7 and pH 9

4. Procedure

4.1 Sample preparation

Grind about 10 g of sample for 60 seconds in the IKA universal mill M20.

Important: Since only very finely ground samples lead to reproducible results, these conditions must be observed strictly.

4.2 Analytical procedure

4.2.1 Weigh out 2.50 g of the sample prepared in accordance with section 4.1 into a 250 ml titration vessel.

4.2.2 Add 60 ml of methanol p.a.

4.2.3 After complete wetting of the sample, add 40 ml of deionized water.

4.2.4 Disperse for 30 seconds using the Ultra-Turrax at a speed of about 18,000 rpm.

4.2.5 Rinse sample particles adhering to the vessel edge and stirrer into the suspension using 100 ml of deionized water.

4.2.6 Condition sample to 25°C in a thermostated water bath (for at least 20 minutes).

4.2.7 Calibrate pH electrode with the buffer solutions pH 7 and pH 9.

4.2.8 The sample is titrated in the Memotitrator DL 70 in accordance with method S 911. If the course of titration is unclear, a duplicate determination is carried out subsequently.

The results printed out are as follows:

pH

V_1 in ml/5 g

V_2 in ml/5g

Principle:

First of all the initial pH of the suspension is measured, then according to the result the pH is adjusted to 6 using KOH or HCl. Then 20 ml of NaCl solution are metered in. The titration is then continued to a pH of 9 using 0.1 N KOH.

Sears numbers:

$$\mathrm{Si-OH + NaCl} \Rightarrow \mathrm{Si-ONa + HCl}$$

$$\mathrm{HCl + KOH} \Rightarrow \mathrm{KCl + H_2O}$$

Calculation

$$V_1 = \frac{V*5}{E}$$

$$V_2 = \frac{V * 5}{E}$$

V_1 = ml KOH or ml HCl to pH 6/5 g of substance

V_2 = ml KOH consumption to pH 9/5 g of substance

E = initial mass

Titraton was conducted on a Memotitrator DL 70 with a switch-off delay time of 2s.

Determining the alkali number:

The alkali number determination, referred to below for short as AN determination, is the consumption of hydrochloric acid in a direct potentiometric titration of alkaline charges or suspensions to a pH of 8.3 (viewed historically: pH 8.3 corresponds to the color change point of phenolphthalein); this gives the free alkali content of the solution or suspension.

The pH meter is calibrated at room temperature, the combined electrode is equilibrated to 40°C, and the sample mixture is then conditioned at 40°C, and on reaching that temperature the titration is conducted.

Because of the fairly long time for equilibrium to be established between the silica/silicate at the specified pH - in this case 8.3 - a waiting time is necessary until the consumption of acid is finally read off. Extensive investigations have found that for the AN determination a waiting time of 15 minutes must be observed, after which the equilibrium has established itself stably and good reproducibility is ensured.

Description of method:

pH meter calibration:

- Calibrating temperature of buffer solutions 20°C
- Temperature equilibration 20°C

Measurement of suspension:

- Temperature equilibration of pH meter at 40°C
- 50 ml of suspension
- 50 ml of distilled water

- Hydrochloric acid c = 0.5 mol/l
- Condition suspension to 40°C
- Determine acid consumption after 15 min titration time
- Titration end at pH 8.3

Accuracy of method: +/- 0.1 ml acid consumption

Determining the maximum choline chloride absorption:

Test means:

A. Test apparatus:

250 ml glass beaker, high form

Spatula

Precision balance

B. Test substances:

75% strength choline chloride solution [choline chloride, ultrapure (Merck)]

Silica under test

Calibration notes

When a new delivery test solution is received, it must be examined comparatively with the quality used up until that time.

Before use, the balances are to be tested for functionality and serviced annually.

Procedure:

10 g of the carrier silica under test are weighed out into a 250 ml glass beaker, high form, and 75% strength choline chloride solution is added dropwise, while stirring with the spatula. The mixture is observed continuously to check when the maximum absorption has been reached. When viewed closely, it is possible to make out white silica particles which stand out distinctly from waxlike (saturated) particles. The maximum choline chloride absorption has been achieved when there are no longer any unladen particles in the mixture and this mixture is not yet waxlike/greasy.

Evaluation:

$$\text{Max. choline chloride absorption in g/100 g} = \frac{(a-10) \times 100}{10}$$

a = total weight

German application 101 12 441.4 filed March 15, 2001 is incorporated herein by reference.

In the invention process, the "metered addition" of aqueous silicate solution and acid may be addition to a pre-existing aqueous silicate solution, or simply to, e.g., an empty vessel (e.g., controlled mixing). The rate of addition of components is guided by the control of the alkali number, and is within the skill of the ordinary artisan in view of the disclosure above.

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